Atom Scattering from Disordered Surfaces in the Sudden Approximation: Double Collisions Effects and Quantum Liquids

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The Sudden Approximation (SA) for scattering of atoms from surfaces is generalized to allow for double collision events and scattering from time-dependent quantum liquid surfaces. The resulting new schemes retain the simplicity of the original SA, while requiring little extra computational effort. The results suggest that inert atom (and in particular He) scattering can be used profitably to study hitherto unexplored forms of complex surface disorder.

Keywords: Atom-solid interaction, Scattering and diffraction

I. INTRODUCTION

Structurally disordered surfaces have been a subject of great interest for some time now. Of special interest are epitaxially grown films, liquid surfaces, and amorphous surfaces. In epitaxial growth for example, metal or semiconductor atoms are adsorbed on a surface under thermal conditions, to form two- and three-dimensional structures on top of it. The physical and chemical properties are determined by the final form of these structures. These may be of dramatic importance, e.g, in the production of electronic devices. One of the most exciting aspects of epitaxial growth kinetics, is that it *creates disordered structures* in the intermediate stages. The disorder manifests itself in the formation of various types of clusters or diffusion limited aggregates on top of the surface. These structures may be monolayers (usually at high temperatures, when the diffusivity is large, or at coverages significantly below one monolayer), in which case the disorder is two-dimensional, or they may be composed of several layers, giving rise to disorder in three dimensions. Epitaxially grown structures of this type offer an exceptional opportunity for both experimental and theoretical studies of disorder. No satisfactory and comprehensive theory of the epitaxial growth process is as of yet available, much due to the absence of reliable interaction potentials for the system. The situation with respect to liquid and amorphous surfaces is similar: very little is known at this point about their structure. Progress at this stage thus hinges critically on data available from experiments. An important experimental technique is thermal atom scattering, and in particular He scattering [1–8]. The main advantage offered by He scattering is complete *surface* sensitivity, as thermal He atoms do not penetrate into the bulk, unlike other scattering techniques such as neutron or X-ray scattering, or LEED. Another important advantage is that He scattering is highly non-intrusive, due to the inertness and low energy of the He atoms. The latter also means that He scattering is really a *diffraction* experiment at the typical meV energy scale at which most experiments are performed, with sensitivity to *atomic-scale* features. The interpretation of He scattering experiments is, however, rather involved due to the complicated interaction between the He atom and the surface.

A highly successful theoretical method in the study of He scattering is the Sudden Approximation (SA), introduced in the context of atom-surface scattering by Gerber, Yinnon and Murrell in 1978 [9]. It is to date one of the most useful tools in the field, and has been reviewed by Gerber [3,6]. While the original formulation of the SA applied to periodic surfaces, it was extended by Gersten *et al.* to deal with scattering from disordered surfaces [10]. The SA was subsequently used to study a large variety of disordered systems, such as isolated adsorbates on crystalline surfaces [11–14], mixed overlayers of Xe+Ar [15,12] and Xe+Kr on Pt(111) [16], randomly corrugated hard walls [17], vacancies and CO adsorbates on Pt(111) [18,19], percolation lattices of substitutionally disordered Xe+Kr monolayers [20], amorphous mixed monolayers and liquids [21], compact islands and diffusion limited aggregates [22–24], and fractals [25,26]. Common to many of these studies was the achievement of detailed insight into the collision dynamics, the prediction and understanding of interesting features in the angular intensity distribution of the scattered atoms. In several cases it was shown that the angular intensity distribution exhibits nonspecular maxima of two types: Several of the peaks are defect-induced rainbows effects, while others (at angles nearer to the specular) are Fraunhofer diffraction interferences. Both types of peaks contain useful, largely complementary, information on defect geometry and on the He/defect interaction. Several further extensions of the SA include the study of Schinke and Gerber which treated phonons and the resulting Debye-Waller attenuation [27]; and Hinch's work [28] which extended the SA to encompass larger parallel momentum transfers.

The main purpose of this work is to extend the SA in two useful directions: the inclusion of double collision processes, and scattering from time-dependent quantum liquid surfaces. Unfortunately, at the time of writing experiments are unavailable for comparison with the results obtained here. The developments will therefore be primarily methodological, in anticipation of experimental data. It is hoped that the results obtained here will motivate He scattering experiments on disordered solid and liquid surfaces. As demonstrated by this work and others before it, He scattering can provide a wealth of information on disordered surface structure and dynamics.

For reasons detailed in Secs. II and III, the SA in its original formulation cannot include double collision events. These, however, are important in many cases, especially when the surface corrugation is large. An analysis of "rainbow" peaks arising due to double collisions and performed here for the first time, shows that these are distinct from single-collision rainbows in that they have an incidence-energy dependence. This should be clearly observable experimentally, e.g., in scattering from CO defects on Pt(111). Multiple scattering by defects has been considered in the past, e.g., by Jónsson, Weare and Levi [29] who derived interesting results concerning the dependence of the specular intensity on coverage for different models of disorder (applied to Xe and CO); by Kara and Armand [30], who considered elastic scattering from a Cu(110) surface covered with randomly distributed copper atoms; A similar multiple scattering theory was presented by Armand and Salanon [31], who showed that for randomly distributed defects, the incoherent cross section is equal to the product of a form factor and a Fourier transform of the two body correlation function of the defects' positions. Common to these works is a multiple scattering expansion of the Lipmann-Schwinger equation for the T-matrix, in powers of the number of He scattering events [29], a perturbation potential due to defects [30], or the number of defects involved in the scattering [31]. The approach to be presented here is somewhat similar to that of [29], in that the He atom is assumed to undergo a second collision. However, the combination of the SA and the Born approximation used here is new, and leads to expressions of significantly greater computational simplicity than that of the general multiple scattering theory.

The study of liquid surfaces is an exciting and novel topic in its own right [32–34], and to date there are very few theoretical methods available for this purpose, in which the surface degrees of freedom are treated classically [8,35]. The extension of the SA that is presented here, in Sec.IV, treats the surfaces as a quantum liquid, within a time-dependent self-consistent-field (TDSCF) approach. This methodological part of the paper serves to generalize the SA to include time-dependent processes and thus renders this useful method significantly more widely applicable. Concluding remarks are brought in Sec.V.

II. BRIEF REVIEW OF THE ORIGINAL SUDDEN APPROXIMATION

Consider a He atom with mass μ incident upon a surface with wavevector $\mathbf{k} = (\mathbf{K}, k_z)$. $\hbar\mathbf{K} = \hbar(k_x, k_y)$ and $\hbar\mathbf{K}'$ are respectively the intial and final momentum components parallel to the surface, and $\hbar k_z$ is the incident momentum normal to the surface. The position of the He atom is $\mathbf{r} = (\mathbf{R}, z)$, where $\mathbf{R} = (x, y)$ is the lateral position. The SA is valid when the collisional momentum transfer $\mathbf{q} = \mathbf{K}' - \mathbf{K}$ in the direction parallel to the surface is much smaller than the momentum transfer normal to the surface: $2k_z \gg |\mathbf{q}|$. This condition is satisfied close to specular scattering and energy $E = (\hbar\mathbf{k})^2/(2m)$, and moderate surface corrugations. When it holds, one can approximately consider the scattering along z as occurring at fixed $\mathbf{R}$. Then if ψ is the He wavefunction, it satisfies a Schrödinger equation where the dependence on $\mathbf{R}$ is *adiabatic*:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dz^2} + V_{\mathbf{R}}(z) \right] \psi_{\mathbf{R}}(z) = E\psi_{\mathbf{R}}(z). \tag{1}$$

Here $V_{\mathbf{R}}(z)$ is the He-surface interaction potential and no inelastic channels are included. This means that each surface point $\mathbf{R}$ gives rise to an elastic real phase shift $\eta(\mathbf{R})$, which can be evaluated in the WKB approximation from Eq.(1) as:

$$\eta(\mathbf{R}) = \int_{\xi(\mathbf{R})}^{\infty} dz \left[\left(k_z{}^2 - \frac{2m}{\hbar^2}V_{\mathbf{R}}(z) \right)^{1/2} - k_z \right] - k_z\,\xi(\mathbf{R}), \tag{2}$$

where $\xi(\mathbf{R})$ is the classical turning point pertaining to the integrand in Eq.(2). The phase shift in turn yields the S-matrix as: $\mathcal{S}(\mathbf{R}) = \exp[2i\eta(\mathbf{R})]$. The $\mathbf{R}$ coordinate is conserved in this picture so the S-matrix is diagonal in the coordinate representation:

$$\langle \mathbf{R}'|\mathcal{S}|\mathbf{R}\rangle = e^{2i\eta(\mathbf{R})}\delta(\mathbf{R}' - \mathbf{R}).$$

Experimentally one measures probabilities $|\mathcal{S}(\mathbf{K} \to \mathbf{K}')|^2$ for $\mathbf{K} \to \mathbf{K}'$ transitions. To obtain these $\langle \mathbf{R}|\mathbf{K}\rangle = \exp(i\mathbf{K}\cdot\mathbf{R})/\sqrt{A}$ (where A is the area of the surface) can be used, to find:

$$\langle \mathbf{K}'|\mathcal{S}|\mathbf{K}\rangle = \int d\mathbf{R}' \, d\mathbf{R} \langle \mathbf{K}'|\mathbf{R}'\rangle \langle \mathbf{R}'|\mathcal{S}|\mathbf{R}\rangle \langle \mathbf{R}|\mathbf{K}\rangle = \frac{1}{A} \int d\mathbf{R} e^{-i\mathbf{q}\cdot\mathbf{R}} e^{2i\eta(\mathbf{R})}. \tag{3}$$

This is the well-known expression for the SA scattering amplitude [9,10].

III. THE ITERATED SUDDEN APPROXIMATION FOR DOUBLE COLLISION EVENTS

A. Background

The SA developed in Sec.II can inherently describe only *single collision* events between the incident particle and the surface. This is because the SA assumes that the momentum transfer in the direction parallel to the surface is much smaller than in the direction perpendicular to it, i.e., the surface is assumed "not too corrugated". A more formal way to see this is by realizing that the SA essentially treats the $\mathbf{R} = (x, y)$ coordinate as *adiabatic*, which implies that each trajectory takes place at constant $\mathbf{R}$. Clearly, no double collisions can occur under such conditions. However, double collisions may take place, e.g., when an incident atom is scattered off a defect onto the surface, or in the opposite order, as depicted in Fig. 1. The purpose of this section is to develop an "Iterated Sudden" (IS) approach, which can be interpreted to include double collision effects as well.

Starting from the first principles of non-relativistic scattering theory, the exact expression for the T-matrix element is [36]:

$$t(\mathbf{k} \rightarrow \mathbf{k}') = \langle \mathbf{k}'|V|\mathbf{k}+\rangle, \tag{4}$$

where $|\mathbf{k}+\rangle = \Omega_+ |\mathbf{k}\rangle$. Here $|\mathbf{k}\rangle$ is the incident state ($t=-\infty$) and Ω_+ is the Møller operator, which propagates $|\mathbf{k}\rangle$ to the state at the time of collision at $t=0$. In the Born approximation it is assumed that $|\mathbf{k}+\rangle \approx |\mathbf{k}\rangle$ [36], which yields $t(\mathbf{k}\rightarrow\mathbf{k}')=\langle \mathbf{k}'|V|\mathbf{k}\rangle$. The IS, on the other hand, consists in setting:

$$|\mathbf{k}+\rangle \approx |\mathbf{k}^{\mathrm{sud}}\rangle \;\; ; \quad |\mathbf{k}^{\mathrm{sud}}\rangle = S^{\mathrm{sud}} |\mathbf{k}\rangle, \tag{5}$$

and where S^{sud} is the S-matrix operator in the SA [Eq.(3)]. Hence:

$$t(\mathbf{k} \rightarrow \mathbf{k}') \approx t^{\mathrm{sud}}(\mathbf{k} \rightarrow \mathbf{k}') = \langle \mathbf{k}'|V|\mathbf{k}^{\mathrm{sud}}\rangle \tag{6}$$

Eq.(6) can be argued to describe a double collision process as follows. In the exact expression Eq.(4), $|\mathbf{k}+\rangle$ represents the actual state at $t = 0$ ("the moment of collision"), as it evolved from $t = -\infty$. However, $|\mathbf{k}^{\mathrm{sud}}\rangle$ is the state at $t = +\infty$,[1] in the SA. Thus Eq.(5) implies setting:

"actual state at collision" = "approximate state much after single collision".

In other words, at the moment of collision, the wave function is taken to have already undergone a prior collision.

A qualitative argument can be given to justify the validity of this approximation. The Lipmann-Schwinger equation for the exact wave function ψ is:

$$\psi = \Phi_{\mathrm{in}} + G_0 \, V \, \psi. \tag{7}$$

Now, an equivalent way to view the IS is by setting $\psi \approx \psi^{\mathrm{sud}}$ in the right-hand side of Eq.(7):

$$\psi = \left[\Phi_{\mathrm{in}} + G_0 \, V \, \psi^{\mathrm{sud}} \right] + G_0 \, V \, \Delta\psi,$$

where $\Delta\psi \equiv \psi - \psi^{\mathrm{sud}}$. Thus by assuming $\psi \approx \psi^{\mathrm{sud}}$, $G_0 \, V \, \Delta\psi$ is neglected. To estimate the magnitude of this term, consider two length-scales: First, it is clear that $G_0 \, V \, \Delta\psi$ is small at *large* distances from the surface, since V becomes small. Secondly, $G_0 \, V \, \Delta\psi$ is also small *close* to the surface, due to the nature of the SA: the SA diagonalizes the Schrödinger equation $(T + V)\psi = E \, \psi$, $E_{ij} = \epsilon_{ii} \, \delta_{ij}$ by taking the energy matrix E to be a *scalar* matrix: $E = \epsilon_0 \, I$, $\epsilon_0 = \max_i \epsilon_{ii}$ [9]. Hence, the SA essentially assumes that the other ($i > 0$) diagonal elements ϵ_i are negligible in comparison to the elements of the diagonalized V. This condition is well satisfied *close* to the surface, where V is largest. Hence one expects $\Delta\psi \approx 0$ to good accuracy for both large and small distances from the surface. Interpolating, one can reasonably expect $G_0 \, V \, \Delta\psi$ to be negligible at *all* distances.

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[1]The Møller operator $\Omega+$ propagates the in-state $|\psi_{\mathrm{in}}\rangle$ to the actual state at $t = 0$. The S operator propagates $|\psi_{\mathrm{in}}\rangle$ to the actual state at $t = +\infty$ [36].

B. Calculation of the T-Matrix Elements

The calculations in this section will be performed in two ways: the first will lead to a result which can be used in numerical simulations, the second will employ some simplifications in order to cast the results in a form amenable to analytic analysis.

1. Wave Function Iterated Sudden

From the close-coupling expansion it follows [10] that the Sudden wave function in the continuum case is:

$$|\psi_{\text{in}}^j(\mathbf{r})\rangle = \int d\mathbf{q}\, |\psi_{\mathbf{q}}^j(\mathbf{r})\rangle,$$

where $j = 1, 2$ depending on whether one is in the classically allowed or forbidden region, and:

$$\langle\mathbf{r}|\psi_{\mathbf{q}}^j(\mathbf{r})\rangle = \Phi_{\mathbf{q}}^j(z)\, e^{i(\mathbf{K}_{\text{in}}+\mathbf{q})\cdot\mathbf{R}}$$

$$\Phi_{\mathbf{q}}^j(z) = \alpha \int d\mathbf{R}\, e^{-i\,\mathbf{q}\cdot\mathbf{R}}\, \Phi_{\mathbf{R}}^j(z)$$

The last equation is where the Sudden approximation is made: $\psi_{\text{in}}^j(\mathbf{r})$ was replaced by $\Phi_{\mathbf{R}}^j(z)$, i.e, the $\mathbf{R}$ coordinate is treated as an adiabatic parameter. This is now further evaluated in the WKB approximation:

$$\Phi_{\mathbf{R}}^j(z) \approx \frac{1}{\sqrt{k(\mathbf{r})}} \exp\left[-i\left(\int_{\xi(\mathbf{R})}^z dz'\, k(\mathbf{R}, z') + \phi^j\right)\right].$$

Here:

$$k(\mathbf{r}) = \sqrt{k_{\text{in}}^{z\,2} - \frac{2\,m}{\hbar^2}V(\mathbf{r})}.$$

In the classically allowed (forbidden) region $\phi^{(1)} = -\pi/4$ and $k(\mathbf{r})$ is real ($\phi^{(2)} = 0$; $k(\mathbf{r})$ is pure imaginary). The normalization ($\langle\psi_{\text{in}}^j|\psi_{\text{in}}^j\rangle = 1$) is found after some algebra:

$$|\alpha| = \frac{1}{(2\pi)^2}\left[\int d\mathbf{r}\, |\Phi_{\mathbf{R}}^j(z)|^2\right]^{-\frac{1}{2}} \approx \frac{1}{(2\pi)^2}\left[\int d\mathbf{r}\, \frac{1}{k(\mathbf{r})}\right]^{-\frac{1}{2}}.$$

Now it is possible to evaluate the matrix element within the IS:

$$t^j(\mathbf{k}_{\text{in}} \to \mathbf{k}_{\text{out}}) = \langle\mathbf{k}_{\text{out}}|V(\mathbf{r})|\psi_{\text{in}}^j\rangle =$$

$$\int d\mathbf{q} \int d\mathbf{r}\, d\mathbf{r}'\, \langle\mathbf{k}_{\text{out}}|\mathbf{r}\rangle\, \langle\mathbf{r}|V(\mathbf{r})|\mathbf{r}'\rangle\, \langle\mathbf{r}'|\psi_{\mathbf{q}}^j(\mathbf{r})\rangle =$$

$$\int d\mathbf{q} \int d\mathbf{r}\, d\mathbf{r}'\, (2\pi)^{-\frac{3}{2}}\, e^{-i\,\mathbf{k}_{\text{out}}\cdot\mathbf{r}}\, [V(\mathbf{r}')\,\delta(\mathbf{r}-\mathbf{r}')]\, \Phi_{\mathbf{q}}^j(z')\, e^{i(\mathbf{K}_{\text{in}}+\mathbf{q})\cdot\mathbf{R}'} =$$

$$\frac{\alpha}{(2\pi)^{\frac{3}{2}}} \int d\mathbf{r}\, V(\mathbf{r})\, e^{-i(\Delta\mathbf{K}\cdot\mathbf{R} + k_{\text{out}}^z z)} \int d\mathbf{R}'\, \Phi_{\mathbf{R}'}^j(z) \int d\mathbf{q}\, e^{i\,\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} =$$

$$\sqrt{2\pi}\,\alpha \int d\mathbf{r}\, V(\mathbf{r})\, e^{-i(\Delta\mathbf{K}\cdot\mathbf{R} + k_{\text{out}}^z z)}\, \Phi_{\mathbf{R}}^j(z). \tag{8}$$

where $\Delta\mathbf{K} \equiv \mathbf{K}_{\text{out}} - \mathbf{K}_{\text{in}}$. Employing the WKB approximation for the wave-function $\Phi_{\mathbf{R}}^z(z)$, one has finally for the transition amplitude from the disordered surface within the IS:

$$t^j(\mathbf{k}_{\text{in}} \to \mathbf{k}_{\text{out}}) =$$

$$\alpha\, e^{i\,\phi^j}\, \sqrt{2\pi} \int d\mathbf{r}\frac{1}{\sqrt{k(\mathbf{r})}}\, V(\mathbf{r})\, \exp\left[-i\left(\int_{\xi(\mathbf{R})}^z dz'\, k(\mathbf{R}, z') + \Delta\mathbf{K}\cdot\mathbf{R} + k_{\text{out}}^z z\right)\right]. \tag{9}$$

Comparing the IS expression (9) to the SA expression (3), note that the computational complexity is essentially increased merely by an additional z-integration. Considering the computational simplicity of the SA, the IS offers an attractive improvement. A further discussion of the physical significance of the IS result is given in Appendix A 1.

Equation (9) is suitable for numerical applications. In order to make further analytic progress, I now develop an alternative, more approximate expression. This will involve calculating the T-matrix element for the IS again, but assuming that *off*-shell (i.e., non energy conserving: $|\mathbf{q}|^2 \neq |\mathbf{q}'|^2$) S-matrix elements are well approximated by *on*-shell ones. The on-shell elements to be used are just the SA elements from Eq.(3). That these are indeed on-shell, follows simply from the fact that Eq.(3) represents the SA result for *elastic* scattering. Starting again from Eq.(6) [standard intermediate steps are omitted from now on for brevity; the details are as in Eq.(8)]:

$$t^j(\mathbf{k}_{\text{in}} \to \mathbf{k}_{\text{out}}) = \langle \mathbf{k}_{\text{out}} | V(\mathbf{r}) \, S^{\text{sud}} | \mathbf{k}_{\text{in}} \rangle =$$
$$\frac{1}{(2\pi)^5} \int d\mathbf{q} \, d\mathbf{q}' \int d\mathbf{R}' \, e^{i\,(\mathbf{K}_{\text{in}} - \mathbf{q}) \cdot \mathbf{R}'} \int d\mathbf{r} \, e^{-i\,(\mathbf{k}_{\text{out}} \cdot \mathbf{r} - k_{\text{in}}^z \, z - \mathbf{R} \cdot \mathbf{q}')} S_{\mathbf{q}'\mathbf{q}} \, V(\mathbf{r})$$

Due to the double integration over the unrestricted intermediate momentum values $\mathbf{q}$, $\mathbf{q}'$, the S-matrix element is off-shell. Approximating $S_{\mathbf{q}'\mathbf{q}}$ by the on-shell expression Eq.(3) yields:

$$t^j(\mathbf{k}_{\text{in}} \to \mathbf{k}_{\text{out}}) \approx$$
$$\frac{1}{(2\pi)^3 A} \int d\mathbf{q} \left(\int d\mathbf{R}' \, e^{i\,(\mathbf{K}_{\text{in}} - \mathbf{q}) \cdot \mathbf{R}'} \, e^{2i\eta(\mathbf{R}')} \right) \int d\mathbf{r} \, V(\mathbf{r}) \, e^{i\,[\mathbf{R} \cdot \mathbf{q} + k_{\text{in}}^z \, z - \mathbf{k}_{\text{out}} \cdot \mathbf{r}]}. \tag{10}$$

And finally:

$$t^j(\mathbf{k}_{\text{in}} \to \mathbf{k}_{\text{out}}) \approx \frac{1}{(2\pi)\,A} \int d\mathbf{r} \, V(\mathbf{r}) \, e^{i\,[2\,\eta(\mathbf{R}) - \Delta\mathbf{k} \cdot \mathbf{r}]}. \tag{11}$$

The last result is the phase-shift equivalent of Eq.(9), in the *on-shell approximation*. This form lends itself more easily to analysis, as will be demonstrated in Sec.III C. Appendix A 2 provides a further discussion of the physical significance of this result.

C. Analysis

In this section I will analyze the expression for the scattering amplitude, including double collisions [Eq.(11)], by considering a simple model potential, of the form:

$$V = V[z - \xi(\mathbf{R})].$$

This is a rather general potential, in that the surface shape function $\xi(\mathbf{R})$ can be chosen arbitrarily. More examples can be found in Ref. [37]. The significance of the $V[z - \xi(\mathbf{R})]$ potential is the following: $z = \xi(\mathbf{R})$ is a two-dimensional surface in real space, and is clearly also an equipotential surface. Thus $z = z_0 + \xi(\mathbf{R})$ defines a continuum of equipotentials as a function of the height z_0 above the surface plane. Hence $V[z - \xi(\mathbf{R})]$ can be interpreted as the potential of a corrugated surface, with $\xi(\mathbf{R})$ representing the corrugation. Now, inserting V into Eq.(11) one obtains:

$$t(\mathbf{k}_{\text{in}} \to \mathbf{k}_{\text{out}}) \propto \int d\mathbf{r} \, e^{i\,(2\eta(\mathbf{R}) - \Delta\mathbf{k} \cdot \mathbf{r})} \, V[z - \xi(\mathbf{R})].$$

Transforming to $\theta = z - \xi(\mathbf{R})$ yields:

$$t(\mathbf{k}_{\text{in}} \to \mathbf{k}_{\text{out}}) \propto \int dx \, dy \, d\theta \, V(\theta) \, e^{i\,[2\eta(\mathbf{R}) - \Delta\mathbf{K} \cdot \mathbf{R} - \Delta k^z\,(\xi(\mathbf{R}) + \theta)]} =$$
$$\underbrace{\int d\mathbf{R} \, e^{i\,[2\eta(\mathbf{R}) - \Delta\mathbf{K} \cdot \mathbf{R} - \Delta k^z\,\xi(\mathbf{R})]}}_{I_{\mathbf{R}}} \int d\theta \, V(\theta) e^{-i\,\Delta k^z\,\theta}. \tag{12}$$

Clearly, only $I_{\mathbf{R}}$ can account for double collisions. To proceed, it is convenient to perform a stationary phase (SP) approximation [38], with the purpose of studying the singularities in the spectrum, i.e., the "rainbow" peaks. The SP yields:

$$\Delta \mathbf{K} = 2\nabla\eta(\mathbf{R}_0) \, - \, \Delta k^z \, \nabla\xi(\mathbf{R}_0), \tag{13}$$

and:

$$|I_{\mathbf{R}}(\Delta \mathbf{K})|^2 \approx (2\pi)^2 \left| 2\frac{\partial^2 \, \eta(\mathbf{R}_0)}{\partial \, \mathbf{R}^2} \, - \, \Delta k^z \, \frac{\partial^2 \, \xi(\mathbf{R}_0)}{\partial \, \mathbf{R}^2} \right|^{-1}.$$

This singularity is a result of the crude SP approximation, and is smoothed out in the full semiclassical expression Eq.(12). However, it provides the condition from which the inflexion point $\mathbf{R}_0$ is found:

$$\left| 2\frac{\partial^2 \, \eta(\mathbf{R}_0)}{\partial \, \mathbf{R}^2} \, - \, \Delta k^z \, \frac{\partial^2 \, \xi(\mathbf{R}_0)}{\partial \, \mathbf{R}^2} \right| = 0. \tag{14}$$

Eqs.(13),(14) together define the *double-collision rainbow* (DCR) condition. After solving for $\mathbf{R}_0$ from Eq.(14), Eq.(13) determines the *position* of the DCR peak. It is similar to the SA rainbow condition [22], $\Delta \mathbf{K} = 2\nabla\eta(\mathbf{R}_0)$. The difference is thus in the second term, with the interesting feature that it depends on the incidence momentum in the normal direction. A direct prediction of the present analysis is therefore that *a DCR peak is distinguished from a single-collision rainbow peak by a positional dependence on incidence energy.* This effect should have a clear experimental signature. Further, the actual position of the peak depends on the corrugation of the surface shape function at the inflexion point. *This position thus provides valuable information on a surface structural parameter.* A more complete analysis, including numerical calculations of the double-collision rainbow intensities, is deferred to a future publication.

IV. TDSCF SUDDEN APPROXIMATION FOR ATOM-SURFACE SCATTERING

In this section I will present a generalized, full derivation of the SA. The derivation is based on the original SA paper [9], and its extension to disordered surfaces [10], but instead of considering the surface atoms as static, they are assumed to be moving under the influence of a time-dependent self consistent field (TDSCF). The result will be a TDSCF-SA, which is presented here for the first time. Applications may include scattering from quantum vibrating solid and liquid surfaces. A similar approach was pioneered by Gerber [35], but with the surfaces degrees of freedom treated classically. A variation on this mixed quantum-classical approach can be found in Ref. [8].

A. Preliminaries

Consider a set of N surface particles moving in a TDSCF, $\mathbf{u}_n = (x_n, y_n)$ being the position of the nth particle, assumed constrained to the surface $z = 0$. Let $f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n, t) = \langle \mathbf{u}_n | \boldsymbol{\kappa}_n \rangle$ be the spatial wavefunction for a surface particle with wavevector $\boldsymbol{\kappa}_n = (\kappa_x^n, \kappa_y^n)$, solving the Schrödinger equation

$$H_n f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n, t) = i\hbar \frac{\partial f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n, t)}{\partial t},$$

with the SCF Hamiltonian $H_n = v_n(\mathbf{u}_n, t) + T_n$, where v_n is the SCF potential for the nth particle and T_n its kinetic operator. A TDSCF separation based on the atoms as the separable degrees of freedom may not be the best, as the residual (their interaction) may become large due to collisions. Nevertheless, for a liquid (the main application I have in mind) no better separable coordinates are known. Moreover, it is possible to switch to lattice modes (phonons) at a later point in the formalism (see below). Now, from the completeness relation for $|\mathbf{u}_n\rangle$ and $|\boldsymbol{\kappa}_n\rangle$,

$$\int d\mathbf{u}_n \, |\mathbf{u}_n\rangle\langle\mathbf{u}_n| = \int d\boldsymbol{\kappa}_n \, |\boldsymbol{\kappa}_n\rangle\langle\boldsymbol{\kappa}_n| = 1,$$

it follows that $f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n, t)$ is orthogonal in both variables:

$$\int d\mathbf{u}_n \, f_{\boldsymbol{\kappa}_n}^*(\mathbf{u}_n, t) f_{\boldsymbol{\kappa}_n'}(\mathbf{u}_n, t) = \langle \boldsymbol{\kappa}_n | \boldsymbol{\kappa}_n' \rangle = \delta(\boldsymbol{\kappa}_n - \boldsymbol{\kappa}_n') \tag{15}$$

$$\int d\boldsymbol{\kappa}_n \, f_{\boldsymbol{\kappa}_n}^*(\mathbf{u}_n, t) f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n', t) = \langle \mathbf{u}_n | \mathbf{u}_n' \rangle = \delta(\mathbf{u}_n - \mathbf{u}_n'). \tag{16}$$

In addition the SCF separation of the surface particles implies:

$$\langle \mathbf{u}_n | \mathbf{u}_{n'} \rangle = \langle \boldsymbol{\kappa}_n | \boldsymbol{\kappa}_{n'} \rangle = \delta_{nn'}.$$

B. Matrix-Diagonalization Sudden (MDS)

Turning attention to the He particle, described by the wavefunction ψ, the time-dependent Schrödinger equation reads:

$$[T + V(\mathbf{R}, z; \{\mathbf{u}_n\}_N; t)]\psi(\mathbf{r}; \{\mathbf{u}_n\}_N; t) = i\hbar \frac{\partial \psi(\mathbf{r}; \{\mathbf{u}_n\}_N; t)}{\partial t}, \tag{17}$$

where $T = (\hbar^2/2\mu)\nabla^2$ the kinetic energy operator of the He particle, V its potential energy which depends on $\{\mathbf{u}_n\}_N$, the positions of the N surface particles. The surface is assumed to be almost frozen during the collision, so that the dependence of V on t is very slow. This time-dependence arises from the slow motion of the surface particles, whose dynamics I wish to include presently, in order to develop a description which accounts for the details of the energy transfer. It should be noted that it is inconceivable at this point to imagine an experiment which is capable of resolving the details of the energy transfer at the level of surface atoms in a liquid, which is thermalized very quickly. However, such experiments may become possible in the future (indeed, efforts are underway in the context of atomic Ar clusters [39]) so that a formalism capable of describing them is desirable.

V and the SCF potentials are not independent; assuming that the influence of the He particle on the surface is small and localized, it should be sufficient to evaluate V at $\mathbf{r} = \mathbf{0}$, thus avoiding the need to find ψ in order to calculate the SCF potentials:

$$v(\mathbf{u}_n, t) = \int \prod_{i \neq n} d\mathbf{u}_i \, f_{\boldsymbol{\kappa}_i}^*(\mathbf{u}_i, t) V(\mathbf{0}; \mathbf{u}_i; t) f_{\boldsymbol{\kappa}_i}(\mathbf{u}_i, t). \tag{18}$$

It is of course possible to average over ψ as well; then Eq.(18) should be regarded as the first iteration in a TDSCF scheme which includes the He particle at later iterations. I now assume that the SCF potentials have been obtained and the problem is the solution of the Schrödinger equation (17). For this purpose it is convenient to expand ψ in a generalized time-dependent close-coupling form:

$$\psi_{\mathbf{k}}(\mathbf{r}; \{\mathbf{u}_n\}_N; t) = \sum_{n=1}^{N} \int d\epsilon \int d\mathbf{q} \int d\boldsymbol{\kappa}_n \, e^{i(\mathbf{q}+\mathbf{K})\cdot\mathbf{R}} f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n, t) \Phi_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}(z) e^{-i(E+\epsilon)t/\hbar}. \tag{19}$$

Here $\hbar\mathbf{k} = \hbar(\mathbf{K}, k_z)$ is the momentum of the incident He particle, $\hbar\mathbf{q} = \hbar(q_x, q_y)$ the momentum transfer parallel to the surface, $E = (\hbar k)^2/(2\mu)$ is the He incidence energy, and ϵ is the energy transfer between the He and the surface. Since periodicity is not assumed, the $\mathbf{q}$'s are unrestricted and continuous. Next the potential is taken to have the form:[2]

$$V(\mathbf{R}, z; \{\mathbf{u}_n\}_N; t) = \sum_{n=1}^{N} V^n(\mathbf{R}, z, \mathbf{u}_n, t) \tag{20}$$

$$V^n(\mathbf{R}, z, \mathbf{u}_n, t) = \sum_{l=1}^{L} V^{nl}(z, t) Q^{nl}(\mathbf{R}, \mathbf{u}_n, t). \tag{21}$$

No restrictions are placed at this point on the functions V^{nl} and Q^{nl} or on their number L, so the expansion is general (more so than in the other derivations of the SA, Refs. [9,10]). It is however assumed, in the spirit of SCF, that the He atom has only two-body interactions with the surface particles. The close-coupling equations will follow from inserting these expressions for ψ and V into the Schrödinger equation (17). Since the surface particles are decoupled by virtue of the SCF approximation, this results in N equations of the form:

$$\int d\epsilon \int d\boldsymbol{\kappa}_n \left[\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \mathbf{R}^2} \right) + \frac{\hbar^2}{2m_n} \frac{\partial^2}{\partial \mathbf{u}_n^2} - \sum_{l=1}^{L} V^{nl}(z, t) Q^{nl}(\mathbf{R}, \mathbf{u}_n, t) + (E + \epsilon) \right] \times$$

$$f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n, t) e^{-i(E+\epsilon)t/\hbar} \int d\mathbf{q} \, e^{i(\mathbf{q}+\mathbf{K})\cdot\mathbf{R}} \Phi_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}(z) = 0, \tag{22}$$

---

[2] n, l are indices, not powers.

where the term $\partial f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n,t)/\partial t$ was neglected with respect to $(E+\epsilon)/\hbar\, f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n,t)$, in accordance with the assumption of slow surface dynamics.

Multiplying throughout by $(\mu/\pi\hbar^2)\exp(-i\mathbf{q}'\cdot\mathbf{R})$ and integrating over $\mathbf{R}$ yields, using $\int d\mathbf{R}\,\exp(i\mathbf{q}\cdot\mathbf{R})=2\pi\delta(\mathbf{q})$:

$$\int d\epsilon\left(\int d\boldsymbol{\kappa}_n\left[\frac{\partial^2}{\partial z^2}-(\mathbf{q}+\mathbf{K})^2+\frac{\mu}{m_n}\frac{\partial^2}{\partial\mathbf{u}_n^2}+k_\epsilon^2\right]f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n,t)\Phi_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}(z)-\right.$$
$$\left.\int d\boldsymbol{\kappa}_n\left[\sum_{l=1}^{L}U^{nl}(z)Q_{\mathbf{q},\mathbf{q}'}^{nl}(\mathbf{u}_n)\right]f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n,t)\Phi_{\epsilon\mathbf{q}'\boldsymbol{\kappa}_n}(z)\right)e^{-i(E+\epsilon)t/\hbar}=0. \tag{23}$$

Here:

$$k_\epsilon^2\equiv\frac{2\mu}{\hbar^2}(E+\epsilon) \tag{24}$$

$$U^{nl}(z,t)\equiv\frac{2\mu}{\hbar^2}V^{nl}(z,t) \tag{25}$$

$$Q_{\mathbf{q},\mathbf{q}'}^{nl}(\mathbf{u}_n)\equiv\frac{1}{2\pi}\int d\mathbf{R}\,e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{R}}Q_{nl}(\mathbf{R},\mathbf{u}_n). \tag{26}$$

Next the orthogonality of the surface particles' wavefunctions is employed to eliminate the integrals over $\boldsymbol{\kappa}_n$ in Eq.(23). Multiplying throughout by $f_{\boldsymbol{\kappa}_n'}^*(\mathbf{u}_n,t)\exp(i(E+\epsilon')t/\hbar)$ and integrating over $\mathbf{u}_n$ and t yields, using Eq.(15):

$$\hbar\left[\frac{\partial^2}{\partial z^2}-(\mathbf{q}+\mathbf{K})^2+k_\epsilon^2\right]\Phi_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}(z)+\int d\boldsymbol{\kappa}_n'\,F_{\epsilon\boldsymbol{\kappa}_n,\epsilon'\boldsymbol{\kappa}_n'}^n\Phi_{\epsilon'\mathbf{q}\boldsymbol{\kappa}_n'}(z)=$$
$$\int d\boldsymbol{\kappa}_n'\,H_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n,\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}^n(z)\Phi_{\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}(z). \tag{27}$$

Here:

$$F_{\epsilon\boldsymbol{\kappa}_n,\epsilon'\boldsymbol{\kappa}_n'}^n\equiv\frac{\mu}{m_n}\int dt\,d\mathbf{u}_n\,f_{\boldsymbol{\kappa}_n'}^*(\mathbf{u}_n,t)\frac{\partial^2}{\partial\mathbf{u}_n^2}f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n,t)e^{i(\epsilon'-\epsilon)t/\hbar}$$

is (up to a constant) a component of the kinetic energy matrix of the nth surface particle associated with an $\epsilon\to\epsilon'$ transition of the He particle, and:

$$H_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n,\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}^n(z)\equiv\sum_{l=1}^{L}U^{nl}(z,t)Q_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n,\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}^{nl} \tag{28}$$

$$Q_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n,\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}^{nl}\equiv\int dt\,d\mathbf{u}_n\,f_{\boldsymbol{\kappa}_n'}^*(\mathbf{u}_n,t)Q_{\mathbf{q},\mathbf{q}'}^{nl}(\mathbf{u}_n)f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n,t)e^{i(\epsilon'-\epsilon)t/\hbar} \tag{29}$$

is a component of the matrix of the Fourier-transformed interaction between the He atom and the nth surface particle. Defining the diagonal "energy operator" $\mathbf{g}_\epsilon^2$ with non-zero components

$$g_{\epsilon\mathbf{q}}^2\equiv k_\epsilon^2-(\mathbf{q}+\mathbf{K})^2, \tag{30}$$

Eq.(27) can be rewritten as follows:

$$\int d\epsilon'\,d\mathbf{q}'\,d\boldsymbol{\kappa}_n'\left[\delta[(\epsilon-\epsilon')/\hbar]\delta(\mathbf{q}-\mathbf{q}')\delta(\boldsymbol{\kappa}_n-\boldsymbol{\kappa}_n')\left(\frac{\partial^2}{\partial z^2}+g_{\epsilon'\mathbf{q}'}^2\right)+\right.$$
$$\delta(\mathbf{q}-\mathbf{q}')F_{\epsilon\boldsymbol{\kappa}_n,\epsilon'\boldsymbol{\kappa}_n'}^n-$$
$$\left.H_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n,\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}^n(z)\right]\Phi_{\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}(z)=0. \tag{31}$$

This can be thought of as the $(\epsilon,\mathbf{q},\boldsymbol{\kappa}_n)$ component of a linear operator equation for the vector $|\Phi^n\rangle$, whose components are the wavefunctions $\Phi_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}(z)$. Clearly then, the He kinetic energy operator on the first line of Eq.(31) is fully diagonal, the nth surface particle kinetic energy operator $\mathcal{F}^n$ on the second line is diagonal in $\mathbf{q}$, and the interaction operator $\mathcal{H}^n$ on the third line is not diagonal. In the Born approximation one essentially retains only the fully diagonal (kinetic) term [36]. Ideally one would like to diagonalize the complete operator acting on $|\Phi^n\rangle$, which would solve the

scattering problem. This is of course unrealistic, and here I will settle for diagonalizing the *interaction* operator. It is to this end that one introduces the Sudden approximation, which is usually written as [9] :

$$2\hbar k_z \gg \hbar|\mathbf{q}|. \tag{32}$$

This implies that the incident momentum in the direction perpendicular to the surface ($\hbar k_z$) is large compared with the momentum transfer for all the channels that significantly contribute to scattering. Here it is necessary to add the assumption:

$$E \gg \epsilon. \tag{33}$$

These conditions are satisfied for most present-day experimental systems. Using Eqs.(32),(33) one can neglect all but the specular term in the energy operator, i.e., assume that:

$$\mathbf{g}_\epsilon^2 \approx g_{0,\mathbf{0}}^2 \mathcal{I} = k_z^2 \mathcal{I}, \tag{34}$$

where $\mathcal{I}$ is the identity operator. Since $g_{\epsilon\mathbf{q}}^2 = k_z^2 - (\mathbf{q}+2\mathbf{K})\cdot\mathbf{q} + 2\mu\epsilon/\hbar^2$, it is seen that the real assumption made is somewhat stronger than Eq.(32):

$$k_z^2 \gg |(\mathbf{q}+2\mathbf{K})\cdot\mathbf{q}|. \tag{35}$$

This implies that the incident beam should be nearly perpendicular to the surface, a condition which is in fact sometimes not met in practice, where the beam is often incident at 45° and the SA calculations have to be corrected accordingly [23,24,40]. The utility of the approximation Eq.(34) is that it will leave the energy operator $\mathbf{g}^2$ diagonal after diagonalization of the interaction operator in Eq.(31). However, whereas this suffices in the stationary surface case, here one is facing also the operator $\mathcal{F}^n$, which is diagonal in $\mathbf{q}$ but not in $\boldsymbol{\kappa}_n$ and ϵ. For this reason it cannot be diagonalized simultaneously with $\mathcal{H}^n$, since to diagonalize this operator it will be necessary to rotate the $\mathbf{q}$ basis and hence introduce $\mathbf{q}$-off-diagonal elements into $\mathcal{F}^n$. Nevertheless the problem can be solved if one assumes as before when $\partial f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n, t)/\partial t$ was neglected, in the spirit of the SA, that *the kinetic energy associated with the surface particles' motion is very small compared to that of the incident He atom.* This is certainly correct for solids, and also a reasonable assumption for liquids at common experimental temperatures. Then it is possible to simply neglect $F_{\epsilon\boldsymbol{\kappa}_n,\epsilon'\boldsymbol{\kappa}_n'}^n$ with respect to k_z^2. With these approximations Eq.(31) becomes, in operator form:

$$\left[\mathcal{I}\left(\frac{\partial^2}{\partial z^2} + k_z^2\right) - \mathcal{H}^n\right]|\Phi^n\rangle = 0. \tag{36}$$

This represents a set of coupled equations for scattering of the He atom by the nth surface particle into the available channels indexed by ϵ, $\mathbf{q}$ and $\boldsymbol{\kappa}_n$. To uncouple the set one needs a unitary matrix $\mathcal{B}^n$ that diagonalizes *all* the (z-independent) $\mathcal{Q}^{nl}$ matrices [whose components are defined in Eq.(29)]. That a single $\mathcal{B}^n$ can diagonalize all L $\mathcal{Q}^{nl}$ matrices is not *a priori* obvious. I will assume for the moment that this is true and come back to it later [see Eq.(42)]. Then:

$$\mathcal{Q}_D^{nl} = \mathcal{B}^n \mathcal{Q}^{nl}(\mathcal{B}^n)^{-1}, \tag{37}$$

with matrix elements

$$\langle\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'|\mathcal{Q}_D^{nl}|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle = \langle\epsilon\mathbf{q}\boldsymbol{\kappa}_n|\mathcal{Q}_D^{nl}|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle\delta(\epsilon - \epsilon')\delta(\mathbf{q} - \mathbf{q}')\delta(\boldsymbol{\kappa}_n - \boldsymbol{\kappa}_n').$$

Since $\mathcal{B}^n$ leaves the energy matrix diagonal in view of Eq.(34), and commutes with purely z-dependent operators, after application of $\mathcal{B}^n$ Eq.(36) becomes:

$$\left[\mathcal{I}\left(\frac{\partial^2}{\partial z^2} + k_z^2\right) - \sum_{l=1}^{L} U^{nl}(z,t)\mathcal{Q}_D^{nl}\right]|\tilde{\Phi}^n\rangle = 0, \tag{38}$$

where

$$|\tilde{\Phi}^n\rangle = \mathcal{B}^n|\Phi^n\rangle.$$

The system of equations (38) is *uncoupled* since the operator acting on $|\tilde{\Phi}^n\rangle$ is now diagonal. Physically, this corresponds to the fact that there are no transitions between the decoupled channels labeled by ϵ, $\mathbf{q}$ and $\boldsymbol{\kappa}_n$ in the new

system. Thus the scattering matrix $\mathcal{S}_D$ that arises from Eq.(38) is diagonal and represents elastic scattering in each of the decoupled channels. Its elements therefore satisfy:

$$\langle \epsilon' \mathbf{q}' \boldsymbol{\kappa}'_n | \mathcal{S}_D^n | \epsilon \mathbf{q} \boldsymbol{\kappa}_n \rangle(t) = e^{2i\eta_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}^n(t)} \delta(\epsilon - \epsilon') \delta(\mathbf{q} - \mathbf{q}') \delta(\boldsymbol{\kappa}_n - \boldsymbol{\kappa}'_n), \tag{39}$$

where $\eta_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}^n(t)$ is the elastic scattering phase shift determined for the $\epsilon\mathbf{q}\boldsymbol{\kappa}_n$ channel from Eq.(38). The time-dependence of the S-matrix element may appear strange (after all the S-matrix describes the entire scattering process from $t = -\infty \to \infty$), but it should be remembered that $\mathcal{S}_D^n$ is not the physical S-matrix; it still needs to be transformed back to the physical frame, which will remove the time-dependence (see below). $\eta_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}^n(t)$ can be evaluated explicitly in the WKB approximation:

$$\eta_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n}^n(t) = \int_{\xi(\epsilon\mathbf{q}\boldsymbol{\kappa}_n;t)}^{\infty} dz \left[\left(k_z^2 - \sum_{l=1}^{L} U^{nl}(z,t) \langle \epsilon\mathbf{q}\boldsymbol{\kappa}_n | \mathcal{Q}_D^{nl} | \epsilon\mathbf{q}\boldsymbol{\kappa}_n \rangle \right)^{1/2} - k_z^2 \right] + k_z \xi(\epsilon\mathbf{q}\boldsymbol{\kappa}_n;t),$$

where $\xi(\epsilon\mathbf{q}\boldsymbol{\kappa}_n;t)$ is the classical turning point associated with the $\epsilon\mathbf{q}\boldsymbol{\kappa}_n$ decoupled channel, i.e., is the z value that solves

$$\sum_{l=1}^{L} U^{nl}(z,t) \langle \epsilon\mathbf{q}\boldsymbol{\kappa}_n | \mathcal{Q}_D^{nl} | \epsilon\mathbf{q}\boldsymbol{\kappa}_n \rangle = k_z^2.$$

To complete the solution of the scattering problem within this *Matrix Diagonalization Sudden* (MDS) approximation, as mentioned above one needs to transform $\mathcal{S}_D^n$ back to the physical scattering matrix $\mathcal{S}^n$. It can be shown that this is accomplished by the inverse unitary transformation [41]:

$$\mathcal{S}^n = (\mathcal{B}^n)^{-1} \mathcal{S}_D^n \mathcal{B}^n. \tag{40}$$

That this transformation removes the time-dependence will be demonstrated explicitly in the coordinate representation Sudden, below. Equations (39)-(40) together provide the amplitude for scattering by the nth surface particle. In the present approach the contributions from all these particles are considered to be additive, so that the full transition amplitude from channel $\epsilon\mathbf{q}$ to $\epsilon'\mathbf{q}'$ is:

$$\langle \epsilon' \mathbf{q}' | \mathcal{S} | \epsilon \mathbf{q} \rangle = \sum_{n=1}^{N} \langle \epsilon' \mathbf{q}' \boldsymbol{\kappa}'_n | \mathcal{S}^n | \epsilon \mathbf{q} \boldsymbol{\kappa}_n \rangle. \tag{41}$$

Note that these are generally complex-valued amplitudes, so that there may be interference between scattering from different surface particles. The representation of the S-matrix as a sum over particles may be questioned. However, since He at typical scattering energies has a wavelength between 0.5Å and 5Å whereas in a liquid the average inter-particle separation is at least on the order of the corresponding solid's lattice constant, i.e., several Å, only at extremely low incidence energies this approximation is expected to break down. This however, is anyway beyond the range of validity of the SA. Moreover, if a representation in terms of lattice modes is required, it can be transformed to by representing the particle displacements in terms of creation (a_i^+) and annihilation (a_i) operators [27]:

$$\mathbf{u}_n = \sum_{i=1}^{N} \left(\boldsymbol{\alpha}_{ni} a_i^+ + \boldsymbol{\alpha}_{ni}^* a_i \right)$$

$$\boldsymbol{\alpha}_{ni} = (2m_n N \omega_i)^{-1/2} \mathbf{e}_i e^{i\mathbf{K}_i \cdot \mathbf{R}_n^{(0)}},$$

where $\mathbf{R}_n^{(0)}$ denotes the equilibrium position of the nth surface atom and ω_i, $\mathbf{K}_i$, and $\mathbf{e}_i$ denote the frequency, wave vector, and polarization vector of mode i, respectively [42].

C. Coordinate Representation Sudden (CRS)

In practice the MDS has almost not been used; instead one can transform to the coordinate representation to obtain the more convenient and popular *Coordinate Representation Sudden* (CRS). To accomplish this it should be noted first that *if they are not truncated*, the $\mathcal{Q}^{nl}$ are trivially diagonal in the coordinate representation, since they are made of matrix elements of the functions $Q^{nl}(\mathbf{R}, \mathbf{u}_n, t)$ [43]. Therefore, in this representation:

$$\langle t\mathbf{R}\mathbf{u}_n|\mathcal{Q}_n^D|t'\mathbf{R}'\mathbf{u}_n'\rangle = Q^{nl}(\mathbf{R},\mathbf{u}_n,t)\delta(t'-t)\delta(\mathbf{R}-\mathbf{R}')\delta(\mathbf{u}_n-\mathbf{u}_n'). \tag{42}$$

At this point it should be clear when a single diagonalizing matrix $\mathcal{B}^n$, required for the MDS, can be found for all $\mathcal{Q}^{nl}$ matrices: since they are all simultaneously diagonal in the coordinate representation if they are not truncated, they all commute, and are therefore simultaneously diagonalizable in any other basis as well. The same reasoning can be applied to the scattering matrix, which was found to be diagonal in the same basis as the $\mathcal{Q}^{nl}$ [Eqs.(37), (39)]. Thus $\mathcal{S}^n$ is also diagonalized by transforming to the coordinate representation:

$$\langle t\mathbf{R}\mathbf{u}_n|\mathcal{S}_D^n|t'\mathbf{R}'\mathbf{u}_n'\rangle = S^n(\mathbf{R},\mathbf{u}_n)\delta(t'-t)\delta(\mathbf{R}-\mathbf{R}')\delta(\mathbf{u}_n-\mathbf{u}_n'). \tag{43}$$

Here $S^n(\mathbf{R},\mathbf{u}_n)$ is found from the solution of the coordinate representation version of Eq.(38) (obtained by inserting the unit operator $\int dt'\,d\mathbf{R}'\,d\mathbf{u}_n'\,|t'\mathbf{R}'\mathbf{u}_n'\rangle\langle t'\mathbf{R}'\mathbf{u}_n'|$ before $|\tilde{\Phi}'\rangle$ and multiplying on the left by $\langle t\mathbf{R}\mathbf{u}_n|$):

$$\left[\left(\frac{\partial^2}{\partial z^2}+k_z^2\right)-V^n(\mathbf{R},z,\mathbf{u}_n,t)\right]\tilde{\Phi}_{t\mathbf{R}\mathbf{u}_n}(z)=0, \tag{44}$$

where $V^n(\mathbf{R},z,\mathbf{u}_n,t)$ was defined in Eq.(21), and $\tilde{\Phi}_{t\mathbf{R}\mathbf{u}_n}(z)=\langle t\mathbf{R}\mathbf{u}_n|\mathcal{B}^n|\Phi^n\rangle$ depends parametrically on t, $\mathbf{R}$ and $\mathbf{u}_n$. Eq.(44) shows that the SA treats the coordinates t, $\mathbf{R}$ and $\mathbf{u}_n$ in an *adiabatic* approximation. One can now write:

$$\langle \epsilon'\mathbf{R}'\mathbf{u}_n'|S_D^n|\epsilon\mathbf{R}\mathbf{u}_n\rangle = e^{2i\eta_\epsilon^n(\mathbf{R},\mathbf{u}_n,t)}\delta(\epsilon-\epsilon')\delta(\mathbf{R}'-\mathbf{R})\delta(\mathbf{u}_n'-\mathbf{u}_n),$$

with the elastic-scattering phase shift evaluated from Eq.(44) in the WKB approximation as:

$$\eta_\epsilon^n(\mathbf{R},\mathbf{u}_n,t) = \int_{\xi(\mathbf{R},\mathbf{u}_n,t)}^\infty dz\,\left[\left(k_z^2-V^n(\mathbf{R},z,\mathbf{u}_n,t)\right)^{1/2}-k_z^2\right]+k_z\xi(\mathbf{R},\mathbf{u}_n,t).$$

Here $\xi(\mathbf{R},\mathbf{u}_n,t)$ is the classical turning point pertaining to Eq.(44). Next, the coordinate representation S-matrix has to be transformed back to the physical one, again using Eq.(40):

$$\langle \epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'|\mathcal{S}^n|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle =$$
$$\int dt'\,d\mathbf{R}'\,d\mathbf{u}_n'\,dt\,d\mathbf{R}\,d\mathbf{u}_n\,\langle \epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'|(\mathcal{B}^n)^{-1}|t\mathbf{R}\mathbf{u}_n\rangle\langle t\mathbf{R}\mathbf{u}_n|\mathcal{S}_D^n|t'\mathbf{R}'\mathbf{u}_n'\rangle\langle t'\mathbf{R}'\mathbf{u}_n'|\mathcal{B}^n|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle. \tag{45}$$

The integrals over the primed variables are eliminated with the help of Eq.(43); in addition one needs the $\mathcal{B}^n$ matrix elements. On the one hand:

$$Q_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n,\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}^{nl} = \langle \epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'|\mathcal{Q}^{nl}|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle =$$
$$\langle \epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'|(\mathcal{B}^n)^{-1}\mathcal{Q}_D^{nl}\mathcal{B}^n|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle =$$
$$\int dt'\,d\mathbf{R}'\,d\mathbf{u}_n'\,dt\,d\mathbf{R}\,d\mathbf{u}_n\,\langle \epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'|(\mathcal{B}^n)^{-1}|t\mathbf{R}\mathbf{u}_n\rangle\langle t\mathbf{R}\mathbf{u}_n|\mathcal{Q}_n^D|t'\mathbf{R}'\mathbf{u}_n'\rangle\langle t'\mathbf{R}'\mathbf{u}_n'|\mathcal{B}^n|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle =$$
$$\int dt\,d\mathbf{R}\,d\mathbf{u}_n\,\{\langle t\mathbf{R}\mathbf{u}_n|\mathcal{B}^n|\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'\rangle\}^*\,Q^{nl}(\mathbf{R},\mathbf{u}_n,t)\,\{\langle t\mathbf{R}\mathbf{u}_n|\mathcal{B}^n|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle\},$$

where the last line follows from Eq.(42) and the unitarity of $\mathcal{B}^n$. On the other hand one has from Eqs.(26),(29):

$$Q_{\epsilon\mathbf{q}\boldsymbol{\kappa}_n,\epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'}^{nl} =$$
$$\frac{1}{2\pi}\int dt\,d\mathbf{R}\,d\mathbf{u}_n\,\left\{f_{\boldsymbol{\kappa}_n',t}(\mathbf{u}_n)e^{-i(\epsilon't/\hbar-\mathbf{q}'\cdot\mathbf{R})}\right\}^*\,Q^{nl}(\mathbf{R},\mathbf{u}_n,t)\,\left\{f_{\boldsymbol{\kappa}_n,t}(\mathbf{u}_n,t)e^{-i(\epsilon t/\hbar-\mathbf{q}\cdot\mathbf{R})}\right\},$$

which shows that $\mathcal{B}^n$ is nothing but the matrix of transformation between the momenta and coordinates:

$$\langle t\mathbf{R}\mathbf{u}_n|\mathcal{B}^n|\epsilon\mathbf{q}\boldsymbol{\kappa}_n\rangle = \frac{1}{2\pi}f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n,t)e^{i\mathbf{q}\cdot\mathbf{R}}e^{-i\epsilon t/\hbar}.$$

Inserting this into Eq.(45) one obtains finally:

$$\langle \epsilon'\mathbf{q}'\boldsymbol{\kappa}_n'|\mathcal{S}_n|j\mathbf{q}\boldsymbol{\kappa}_n\rangle =$$
$$\frac{\alpha}{4\pi^2}\int dt\,d\mathbf{R}\,d\mathbf{u}_n\,\left\{f_{\boldsymbol{\kappa}_n'}^*(\mathbf{u}_n,t)e^{-i(\mathbf{q}'\cdot\mathbf{R}-\epsilon't/\hbar)}\right\}e^{2i\eta_\epsilon^n(\mathbf{R},\mathbf{u}_n,t)}\left\{f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n,t)e^{i(\mathbf{q}\cdot\mathbf{R}-\epsilon t/\hbar)}\right\}, \tag{46}$$

for the amplitude to scatter off the nth surface particle, accompanied by a momentum transfer $\hbar\mathbf{q} \to \hbar\mathbf{q}'$ and energy transfer $\epsilon_j \to \epsilon'$ by the He atom, and a change $\hbar\boldsymbol{\kappa}_n \to \hbar\boldsymbol{\kappa}'_n$ in the momentum of the surface particle. As in the MDS, the full amplitude for the scattering of the He atom is given by the sum over all surface particles, Eq.(41). The normalization factor α is found from the conservation of the total scattering probability:

$$\sum_n \int d\epsilon' \, d\mathbf{q}' \, d\boldsymbol{\kappa}'_n |\langle \epsilon'\mathbf{q}'\boldsymbol{\kappa}'_n|\mathcal{S}_n|j\mathbf{q}\boldsymbol{\kappa}_n\rangle|^2 = 1. \tag{47}$$

This completes the derivation of the TDSCF-SA, which is given in final form by Eqs.(41), (46) and (47). *The novel feature in the present result is the appearance of the time dependence and the explicit accounting for the change undergone by the surface particles*; for comparison see again the usual SA expression Eq.(3).

The time dependence in Eq.(46) can be made even more explicit by expanding the wave function of the surface particle in terms of its energy eigenstates:

$$|\boldsymbol{\kappa}_n\rangle = \sum_{j_n} c_{j_n} |j_n\rangle e^{-iE_{j_n}t/\hbar},$$

or, by multiplying on the left by $\langle\mathbf{u}_n|$, in the coordinate representation:

$$f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n;t) = \sum_{j_n} c_{j_n} \phi_{j_n}(\mathbf{u}_n) e^{-iE_{j_n}t/\hbar},$$

where $\phi_{j_n}(\mathbf{u}_n) = \langle\mathbf{u}_n|j_n\rangle$. Plugging this into Eq.(46) one obtains the matrix element:

$$\langle\boldsymbol{\kappa}'_n|e^{2i\eta^n_\epsilon(\mathbf{R},\mathbf{u}_n,t)}|\boldsymbol{\kappa}_n\rangle \equiv \int d\mathbf{u}_n \, f^*_{\boldsymbol{\kappa}'_n}(\mathbf{u}_n;t) e^{2i\eta^n_\epsilon(\mathbf{R},\mathbf{u}_n,t)} f_{\boldsymbol{\kappa}_n}(\mathbf{u}_n;t)$$

$$= \sum_{j_n,j'_n} c'^*_{j'_n} c_{j_n} \, e^{i(E_{j'_n}-E_{j_n})t/\hbar} M_{j'_n j_n}(\mathbf{R},t), \tag{48}$$

where:

$$M_{j'_n j_n}(\mathbf{R},t) = \int d\mathbf{u}_n \, \phi^*_{j'_n}(\mathbf{u}_n) e^{2i\eta^n_\epsilon(\mathbf{R},\mathbf{u}_n,t)} \phi_{j_n}(\mathbf{u}_n).$$

The $M_{j'_n j_n}$ are the $\mathbf{R}$-dependent amplitudes for a transition from energy eigenstate $|j_n\rangle$ to $|j'_n\rangle$ for the nth surface particle in the "t^{th}" configuration. The off-diagonal elements, with $j'_n \neq j_n$, correspond to inelastic transitions due to the collision with the He atom, as can be seen by the presence of the oscillatory term with the $E_{j'_n} - E_{j_n}$ factor in Eq.(48). *This demonstrates explicitly how the TDSCF-SA accounts for energy transfer from/to the liquid surface.* The $M_{j'_n j_n}$ have been calculated analytically (under certain simplifying assumptions) for the harmonic oscillator case by Schinke and Gerber [27], where they give rise to the Debye-Waller factor. The present formulation is more general as it is not restricted to phonons, and explicitly includes the energy transfer to/from the He atom. This novel feature should make the present result useful in a comparison with inelastic He scattering data from liquids, to be undertaken in a future publication.

V. SUMMARY AND CONCLUSIONS

This paper has introduced two novel extensions of the Sudden Approximation (SA) for atom scattering from surfaces, namely: (1) scattering in the presence of double collisions between the impinging atom and the surface (the Iterated Sudden: IS), and (2) scattering from a time-dependent quantum liquid surface (the time-dependent self consistent field SA: TDSCF-SA).

The IS is a natural generalization of the SA, which takes double-collision events between the atom and the surface into account. An exact version was presented, suitable primarily for numerical applications, along with a more approximate version, which can be used for analytical work. The exact version is only slightly more computationally expensive than the original SA. It was shown that the IS predicts the presence of new rainbow peaks in the angular intensity distribution, which arise due to double collisions, and are absent in the SA. These rainbow peaks can be experimentally distinguished from those arising from single-collisions by their dependence on incidence energy. The IS seems to properly generalize the SA, which was the goal in its derivation. It is of interest to apply the IS to a

realistic problem, e.g. a CO adsorbate on a Pt(111) surface, and compare the IS predictions to those of the SA and exact calculations.

The TDSCF-SA generalizes the SA by taking into account the dynamics of the surface particles. The latter are treated as independent, with each particle moving in an average potential determined by all the others, and the incident atom. The resulting expression for the scattering amplitude depends on the energy transfer between the incident atom and the surface, and it is this inelastic contribution which constitutes the main generalization of the original SA approximation. The TDSCF-SA could find applications in simulations related to the novel experiments on inert atom scattering from molten metal liquid surfaces, such as those by Nathanson and co-workers [32–34].

Theoretical applications of the methods developed here will be undertaken in the future, but it is hoped above all that this work will stimulate experimentalists to further utilize inert atom scattering in the study of increasingly complex surface disorder. The results presented here suggest that such experiments can reveal a wealth of information concerning disordered surface structure, be it in the atomic-level details of isolated adsorbates, the dynamics and time-dependent structure of quantum liquid surfaces, or the statistics of randomly corrugated surfaces.

ACKNOWLEDGEMENTS

APPENDIX A: CONNECTION OF THE ITERATED SUDDEN EXPRESSIONS WITH THE SINGLE-COLLISION CASE

1. Wave-Function Iterated Sudden

It is interesting to rewrite Eq.(9) in a form which makes the connection with the single-collision case, i.e., the ordinary SA, more transparent. Equation (8) can be rewritten as:

$$
t^j(\mathbf{k}_{\text{in}} \to \mathbf{k}_{\text{out}}) =
\frac{\alpha}{(2\pi)^{\frac{3}{2}}} \int d\mathbf{q} \int d\mathbf{r}\, e^{i\,[(\mathbf{K}_{\text{in}} - \mathbf{q})\cdot\mathbf{R} - k_{\text{out}}^z z]}\, \Phi_\mathbf{R}^j(z) \int d\mathbf{R}'\, V(\mathbf{R}', z) e^{i\,[(\mathbf{q} - \mathbf{K}_{\text{out}})\cdot\mathbf{R}']}. \tag{A1}
$$

The first term in the last expression is, up to a constant factor, exactly the transition amplitude from a Sudden state $|\psi_{\text{in}}^j\rangle$ to an *intermediate* state $\langle \mathbf{q}, k_{\text{out}}^z|$, as is shown next by calculating the $\langle \mathbf{q}, k_{\text{out}}^z|$ component of the SA wave-function:

$$
\langle \mathbf{q}, k_{\text{out}}^z|\psi_{\text{in}}^j\rangle = \int d\mathbf{r}\, \langle \mathbf{q}, k_{\text{out}}^z|\mathbf{r}\rangle \langle \mathbf{r}|\psi_{\text{in}}^j\rangle =
$$

$$
\int d\mathbf{q}' \int d\mathbf{r}\, \Phi_{\mathbf{q}'}^j(z)\, e^{i\,(\mathbf{K}_{\text{in}} + \mathbf{q}')\cdot\mathbf{R}}\, e^{-i(\mathbf{q}, k_{\text{out}}^z)\cdot\mathbf{r}}\, (2\pi)^{-\frac{3}{2}} =
$$

$$
\sqrt{2\pi}\, \alpha \int d\mathbf{r}\, \Phi_\mathbf{R}^j(z)\, e^{i\,[(\mathbf{K}_{\text{in}} - \mathbf{q})\cdot\mathbf{R} - k_{\text{out}}^z z]},
$$

which is indeed the term mentioned above. Having verified this, the double-collision expression obtained within the IS, Eq.(A1), can be interpreted as the transition amplitude from an initial state $|\psi_{\text{in}}^j\rangle$ (after a first collision) into an intermediate state $\langle \mathbf{q}, k_{\text{out}}^z|$, multiplied by a Born-type propagator $P \equiv \int d\mathbf{R}'\, V(\mathbf{R}', z) \exp\left[i\left((\mathbf{q} - \mathbf{K}_{\text{out}}) \cdot \mathbf{R}'\right)\right]$, which takes the particle to the final state $\langle \mathbf{k}_{\text{out}}|$ (after a second collision), integrated over all intermediate diffraction vectors $\mathbf{q}$. The "propagator" P depends on z through $V(\mathbf{R}', z)$. Thus the first and second collisions are coupled not only by the intermediate momentum vector, but also by the (non-adiabatic) z-coordinate. As shall be shown shortly, this coupling is closely connected to the distinction between off-shell and on-shell amplitudes, and can be used to determine when an off-shell amplitude can be approximated by an on-shell one.

2. Phase-Shift Iterated Sudden

Consider Eq.(10): the expression in parentheses is, according to Eq.(3), just $\langle\mathbf{q}|S^{\text{sud}}|\mathbf{K}_{\text{in}}\rangle$, i.e., the single collision amplitude for the transition from $|\mathbf{K}_{\text{in}}\rangle$ to the intermediate state $\langle\mathbf{q}|$, in the SA. Thus Eq.(10) can be interpreted as expressing the transition amplitude from an initial state $|\mathbf{K}_{\text{in}}\rangle$ to a final state $|\mathbf{k}_{\text{out}}\rangle$, after passing through an intermediate state $|\mathbf{q}\rangle$. The expression in parentheses in Eq.(10) then expresses the first collision, which is subsequently multiplied by a Born type propagator, expressing the second collision: the transition from $\langle\mathbf{q}|$ to $|\mathbf{k}_{\text{out}}\rangle$. But as opposed to the situation in the Wave-Function expression Eq.(A1), the two collision events in Eq.(10) are *decoupled* in the z-direction. This is due to the on-shell approximation used in deriving in Eq.(10). Hence one would expect an on-shell approximation to be valid as long as the behavior of the particle in the z-direction is primarily determined by the initial z-component of the particle's wave-vector. For in this case, the influence of the potential on the propagation in the z-direction is relatively negligible. This is in the spirit of the high-energy SA.

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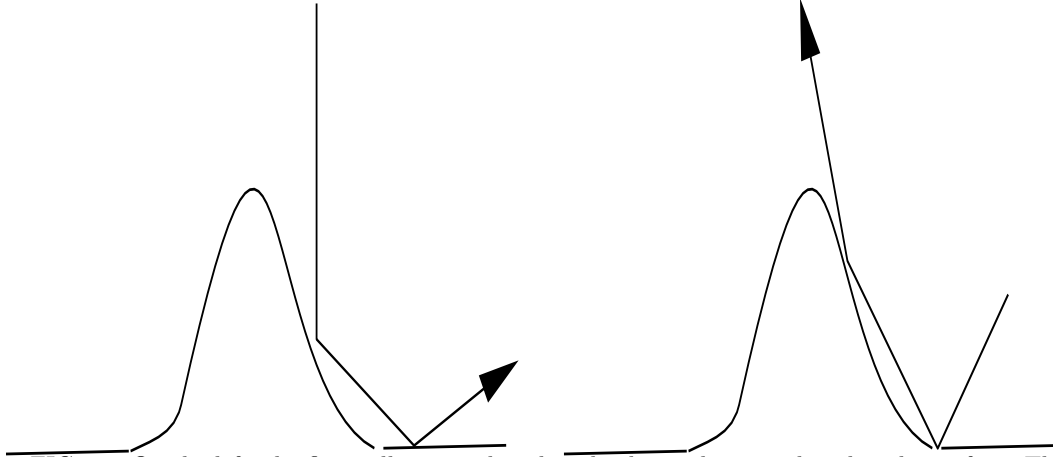

FIG. 1.   On the left, the first collision strikes the adsorbate, the second strikes the surface. The reverse sequence occurs on the right.